COUCLES OF THE

15

20

25

30

35

WO 99/25673

Unsaturated palm oil fatty alcohols

Field of the invention

The invention relates to unsaturated fatty alcohols which are obtained by fractionating palm oil fatty acid methyl esters, and then hydrogenating the fraction of unsaturated long-chain methyl esters, and to a process for the preparation of these fatty alcohols.

10 Prior art

fatty alcohols important Unsaturated are intermediates for a large number of products of the chemical industry, such as, for example, for the preparation of surfactants and skincare products. review on this topic can be found, for example, by U. Ploog et al. in Seifen-Öle-Fette-Wachse [Soaps-Oils-Fats-Waxes] 109, 225 (1983). They are prepared from more or less unsaturated fatty acid methyl esters which can be hydrogenated, for example, in the presence of chromium- or zinc-containing mixed catalysts [Ullmann's Encyclopedia of Industrial Chemistry, Verlag Chemie, Weinheim, 4th Edition, Vol. 11, p. 436 ff]. The prior art is a large-scale process, as has hitherto also been carried out by the applicant, according to which animal fats and oils are used, and the unsaturated fatty alcohols produced after the hydrogenation are distilled at a still temperature of e.g. 220 to 250°C and a reduced pressure of from 1 to 20 mbar - measured at the top of the column. Since the preparation of unsaturated is associated with high fatty alcohols distillation has been carried out with as low a raw material loss as possible. In fact, in this way, it was possible to achieve a yield of about 90% of theory, and correspondingly a loss of 10%, although the products intrinsic odor. Α marked exhibited а disadvantage is that the fatty alcohols of the prior art have unsatisfactory storage and low-temperature behavior.

15

20

25

unsaturated fatty application reasons, alcohols having iodine numbers of from 50 to 80 are have these since preferred particularly solidification point which is favorable for use cosmetic products. Unsaturated fatty alcohols having abovementioned range numbers in the currently largely based on animal raw materials. The desired iodine number range is set by blending differing iodine having different products the iodine number ranges. Adjustment of range distillative methods is not possible since the iodine number or iodine number range of animal-based fatty acids or fatty alcohols remains virtually constant during fractionation. However, animal fats have the a very heterogeneous disadvantage that they have structure. For example, animal fats contain nitrogencontaining compounds, such as amides or steroids, such as, for example, cholesterol, which are directly or abovementioned the for responsible indirectly products. The the of odor unpleasant containing compounds can become involved in secondary impairs product stability, which particular oxidation stability, and leads to discolored products. In addition, because of the continuing BSE debate, products which are prepared using beef tallow are viewed extremely critically by the consumer. In the cosmetics market, there is therefore a continuous need for ever purer raw materials of ever higher quality, a demand which can usually only be met by ever more and additional industrial processes complex 30 purification steps. In the case of unsaturated fatty in particular, the need there is, alcohols, products having improved color and odor quality and a more advantageous low-temperature behavior. Added to this is the fact that in recent years consumer behavior 35 has changed to the effect that consumers place very great value on purely vegetable products. The known vegetable fatty alcohols have iodine numbers in the range below 20 or very high iodine numbers above 100.

15

20

25

30

Fatty alcohols having iodine numbers in the abovementioned range between 20 and 95, which is particularly preferred with regard application to technology, are not known. The blending of fatty alcohols having very different iodine numbers does not products. to satisfactory German Laid-open Specification DE-A1 4335781 (Henkel) discloses process in which the triglycerides present in the vegetable fats or raw materials are firstly cleaved by pressurized cleavage into glycerol and fatty acids, and latter are esterified with methanol, starting materials are directly transesterified to give the fatty acid methyl esters and then the esters are hydrogenated to give the alcohols, either the fatty acid methyl esters or the hydrogenation products being fractionated by removal of an amount of forerunnings such that the end product has an iodine number of from 20 to 110 and a conjuene content of less than 4.5% by weight. Whilst the process can be used for vegetable raw materials such as palm oil for the preparation of unsaturated fatty alcohols in the iodine number range 50 to 65 without problems, if palm oil is used to produce unsaturated fatty alcohols in the iodine number range from 65 to 85, results are obtained which are surprisingly not entirely satisfactory.

The object of the present invention consequently to provide unsaturated fatty alcohols based on palm oil which have iodine numbers in the range from 65 to 85 and, compared with animal-based unsaturated fatty alcohols, have greater stability and comparable or better low-temperature behavior. The aim was also to obtain extremely pure coupled products.

Description of the invention

35 The invention provides unsaturated palm oil fatty alcohols having an iodine number in the range from 65 to 85, which essentially comprise unsaturated fatty alcohols and mixtures of saturated fatty alcohols of the formula (I)

20

25

 R^1OH (I)

in which R¹ is a saturated or unsaturated, linear or branched alkyl radical having 14 to 20 carbon atoms, obtainable by

- (a) fractionating palm oil fatty acid methyl esters into a predominantly saturated C_{16} distillate and a predominantly unsaturated $C_{16/18}$ bottom product, and
- 10 (b) hydrogenating the bottom product with retention of the double bonds to give the corresponding alcohols.

have found that, Surprisingly, we by process according to the invention, it is now possible first time to obtain unsaturated alcohols, even those based on palm oil, in the iodine number range from 65 to 85 and which have good color and oxidation stability and excellent low-temperature behavior; additionally, the products are virtually odorless. A further advantage is that a very pure palmitic acid methyl ester fraction is obtained as an intermediate, which further processed can be separately.

The invention further provides a process for the preparation of unsaturated palm oil fatty alcohols having an iodine number in the range from 65 to 85, which essentially comprise unsaturated fatty alcohols and mixtures of saturated fatty alcohols of formula (I)

30 R¹OH (I)

in which \mathbb{R}^1 is a saturated or unsaturated, linear or branched alkyl radical having 14 to 20 carbon atoms, in which

35 (a) palm oil fatty acid methyl esters are fractionated into a predominantly saturated C_{16} distillate and a predominantly unsaturated $C_{16/18}$ bottom product, and

(b) the bottom product is hydrogenated with retention of the double bonds to give the corresponding alcohols.

Fractionation

5

10

15

20

25

30

35

The fractionation of the palm oil fatty acid carried out methyl esters can be batchwise continuously at reduced pressure. Heating can, for example, be by means of superheated steam, a still temperature of e.g. 220 to 250°C normally prevailing. The actual fractionation takes place in a packed column low-pressure-loss containing internals. Suitable internals are, for example, arranged sheet-metal packings. Other examples can be found in RÖMPP Chemie Lexikon, Thieme Verlag, Stuttgart, 9th Edition, Vol. 3, p. 2305 (1990) under the heading "Kolonnen-Einbauten" [Column internals] and in the literature cited therein. The required fine vacuum of 1 to 20 mbar at the top of the column can be achieved, for example, using waterring pumps and upstream steam jets. The pressure drop over the entire distillation unit should preferably be 20 mbar. distillate more than Α containing predominantly saturated C16 portions and a bottom containing predominantly unsaturated C16-C18 product portions are obtained in the process. The weight ratio of distillate to bottom product is in the range from 30:70 to 35:65.

Hydrogenation

The subsequent hydrogenation of the predominantly unsaturated methyl ester fraction obtained as bottom product with retention of the double bonds can be carried out in a manner known per se, i.e. for example in the presence of commercially available zinc/chromium catalysts, at temperatures in the range from 250 to 350°C and a hydrogen pressure of from 200 to 275 bar. The conjuene content of the products is in the range from 6 to 12% by weight, and the content of hydrocarbons is below 3% by weight, preferably below 1% by weight.

10

Industrial applicability

unsaturated palm oil fatty alcohols obtained by the process according to the invention are low in color and odor and have a particularly low-temperature behavior. They advantageous therefore suitable as raw materials for the preparation of washing, rinsing and cleaning products, and also products for hair care and body care, in which they can be present in amounts of from 1 to 50% by weight, 30% by weight, based on preferably 5 to compositions.

10

15

A technical-grade palm oil fatty acid methyl ester was fractionated in a packed column containing low-pressure-loss internals at a still temperature of 200°C and a head vacuum of 20 mbar, 30% by weight of acid palmitic methyl ester being produced distillate, while in the still 70% by weight of a $C_{16/18}$ fatty acid methyl ester mixture remained, which had an iodine number of 74. The ester mixture from the still was transferred to an autoclave and reduced therein in the presence of commercially available zinc/chromium catalysts at 300°C and 250 bar with hydrogen to give mixture of the corresponding alcohols. hydrogenation product from freed methanol had, according to gas-chromatographic and wet-chemical analysis, the following characteristics:

Characteristics for the hydrogenation product

Characteristics for the hydrogenation product			
Composition	Portion	Specification	Value
	[area %]		
Cetyl	18.3	Iodine number	74
alcohol			
Palmoleyl	0.5	Hydroxyl	212
alcohol		number	
Margarinyl	0.6	Acid number	0.02
alcohol	·		
Stearyl	8.5	Saponification	0.4
alcohol		number	
Oleyl	61.2	Hazen color	10
alcohol		number	
Linolyl	3.3	Conjuene	6.6% by wt.
alcohol		content	
Linolenyl	6.7	Solidification	22.7°C
alcohol		point	
Hydrocarbons	0.9		